ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Catalysis A: General 275 (2004) 87–93

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Epoxidation of styrene by anhydrous *t*-butyl hydroperoxide over gold supported on Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3

N.S. Patil[a,b], R. Jha[a], B.S. Uphade[a], S.K. Bhargava[b], V.R. Choudhary[a,*]

[a]*Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune 411008, India*
[b]*Department of Applied Chemistry, RMIT University, Melbourne 3000, Australia*

Received 19 January 2004; received in revised form 6 July 2004; accepted 21 July 2004
Available online 2 September 2004

Abstract

Group IIIa metal (viz. Al, Ga, In and Tl) oxide-supported gold nanoparticles, prepared by deposition–precipitation (DP) using NaOH and by homogeneous deposition–precipitation (HDP) using urea, were employed as highly active/selective and reusable catalysts for the epoxidation of styrene (at 82 °C) by anhydrous *t*-butyl hydroperoxide (TBHP). The loading and average particle size of gold, when it was deposited on the Gr. IIIa metal oxides by the HDP, was found to increase in the following order: Al_2O_3 (6.36 wt.%, 4.1 $\pm$ 2.3 nm) $<$ Ga_2O_3 (6.43 wt.%, 6.67 $\pm$ 3.7 nm) $<$ In_2O_3 (6.81 wt.%, 15.6 $\pm$ 6.3 nm) $<$ Tl_2O_3 (8.00 wt.%, 24.4 $\pm$ 13.1 nm). Both the activity and the epoxide selectivity of the supported gold catalysts are in the following order: $Au/Al_2O_3 < Au/Ga_2O_3 < Au/In_2O_3 < Au/Tl_2O_3$. Using the DP method, the Au loading on Al_2O_3 and Tl_2O_3 was found to be 2.10 and 5.42 wt.%, respectively, such values are much lower than those achieved by the HDP method. The Al_2O_3, Ga_2O_3 and In_2O_3 supports alone showed little or no epoxidation activity/selectivity. However, the Tl_2O_3 support alone showed the activity and epoxide selectivity comparable to that of the Au/Tl_2O_3 catalysts. The surface species on the Au/Al_2O_3 were found to be only metallic gold (Au^0) ones and Al in single oxidation state (Al^{3+}). However, the surface species on the Au/In_2O_3 were both the metallic and ionic gold (Au^0 and Au^{3+}) and the indium in two oxidation states ($In^{3+}$and In^{2+} or In^{1+}). The gold loading and both the epoxidation activity and selectivity are increased with increasing the basicity and/or reduction potential of the support used in the supported Au catalysts.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Epoxidation of styrene; Styrene oxide; *t*-Butyl hydroperoxide; Gold supported on Gr. IIIa metal oxides

1. Introduction

Styrene oxide is an important organic intermediate in the synthesis of fine chemicals and pharmaceuticals. It is traditionally produced by epoxidation of styrene using stoichiometric amounts of peracids as an oxidising agent [1]. However, peracids are very expensive, hazardous to handle, non-selective for the epoxide formation and also lead to formation of undesirable products, creating a lot of waste. In order to overcome these limitations, a few studies have been reported on the epoxidation of styrene over environ-friendly solid catalysts viz. Ti/SiO_2 [2–4], TS-1 [4–7], Ti-MCM-41 [7], Fe or V/SiO_2 [4], TBS-2, TS-2 [8] and γ-Al_2O_3 [9] catalysts, using TBHP [2], H_2O_2 [3–5,7–9] or urea–H_2O_2 adduct [6], as an oxidizing agent. With H_2O_2 as an oxidizing agent, although the styrene conversion was very high, the selectivity for styrene oxide was very poor. On the other hand, with TBHP [2] and urea–H_2O_2 adduct [6] as oxidizing agents, high styrene oxide selectivity (>80%) was observed, but only at a low styrene conversion (9.8 and 17.7%, respectively). It is, therefore, important to develop a novel reusable solid catalyst, to achieve high styrene conversion particularly at high styrene oxide selectivity in the epoxidation of styrene.

Epoxidation of terminal olefin, such as styrene, is relatively difficult and hence requires prolonged reaction

---

* Corresponding author. Tel.: +91 20 25893300; fax: +91 20 25893041.
E-mail address: vrc@ems.ncl.res.in, vrc@che.ncl.res.in (V.R. Choudhary).

0926-860X/\$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2004.07.023

times [10]. Recently, growing attention is paid to the direct gas phase oxidation of propylene to propylene oxide by mixed H_2 and O_2 over Au supported on TiO_2, TiO_2/SiO_2 and Ti-containing zeolites [11–13]. Therefore, it is an interesting to explore the possibility of using supported gold catalysts also for the liquid phase selective epoxidation of styrene to styrene oxide. The present work was undertaken with the objective of investigating the styrene epoxidation reaction using gold deposited on Gr. IIIa metal oxide (viz. γ-Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3) supports as a catalyst. To the best of our knowledge, no work on Au supported on Ga_2O_3, In_2O_3 or Tl_2O_3 has been reported so far. Gold was deposited on the supports by a homogeneous deposition–precipitation (using urea) method and also in a few cases by a deposition–precipitation (using sodium hydroxide) method. An anhydrous *t*-butyl hydroperoxide (TBHP) was used as an oxidising agent in the epoxidation of styrene, without using any solvent.

2. Experimental

2.1. Catalyst preparation and characterization

The γ-Al_2O_3 was obtained by calcining bohemite (γ-AlOOH) at 500 °C for 4 h in air. Ga_2O_3 (Aldrich) and In_2O_3 (Aldrich) were used as received. Tl_2O_3 was obtained by hydrolysing thallus acetate (Aldrich) in aqueous ammonia (30%), washing the resulting metal hydroxide, filtering it and then calcining it at 500 °C for 4 h in air. The crystal phases of the metal oxide supports were confirmed by XRD. Gold was deposited on the Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3 by homogeneous deposition–precipitation (HDP) method, using urea as the precursor for precipitating agent (ammonium hydroxide) [14–16] and on the Al_2O_3 and Tl_2O_3 supports by deposition–precipitation (DP) method, using NaOH [17], as follows.

2.1.1. Deposition of gold by DP method

The Au/Al_2O_3 (DP) and Au/Tl_2O_3 (DP) catalysts were prepared by contacting the respective support under stirring with aqueous NaOH solution containing $HAuCl_4{\cdot}3H_2O$ (Thomas Baker Chem. Ltd., Mumbai, India) at a pH of 7.0 and 70 °C for 1 h, aging the mixture at 30 °C for 1 h, filtering and thoroughly washing the solid with deionized water, drying and calcining the dried solid in air at 400 °C for 2 h [17].

2.1.2. Deposition of gold by (HDP) method

The Au/Al_2O_3 (HDP), Au/Ga_2O_3 (HDP), Au/In_2O_3 (HDP) and Au/Tl_2O_3 (HDP) catalysts were prepared by the HDP method described elsewhere [16]. In a typical procedure, the metal oxide support (2.0 g) was contacted under stirring with aqueous urea (5.19 g) solution containing $HAuCl_4{\cdot}3H_2O$ (0.32 g). The temperature of the reaction mixture was gradually increased up to 95 °C and was maintained for 6 h. Thereafter, the mixture was aged at 30 °C for 12 h and then the solid was filtered, thoroughly washed with deionised water, dried at 90 °C for 12 h and finally calcined at 400 °C for 2 h.

The catalysts were characterized for their Au content by ICP-OES (using Perkin-Elmer Analyser), for their Au particle size by HRTEM (at 200 kV using a JEOL 1200 EX using CCD camera) and also for their surface species by XPS (using a Fisons VG310F Scanning Auger Nanoprobe). The surface areas of the supports and the catalysts were measured by the single point N_2 adsorption method (using a surface area analyser, Quanta Chrome, USA).

2.2. Catalytic activity

The styrene epoxidation reactions over the supported Au catalysts and also over the supports (without gold) were carried out at atmospheric pressure by contacting 0.1 g catalyst (or support) with 1.2 ml (10 mmol) styrene and 5.7 ml (15 mmol) anhydrous *t*-butyl hydroperoxide [TBHP (26%) in benzene] in a magnetically stirred glass reactor (capacity: 10 cm^3), under reflux (at 82–83 °C) for a period of 3 h. After the reaction mixture was cooled, the catalyst was separated from the reaction mixture by filtration. The reaction products and unconverted reactants were analysed by GC with FID using SE-30 column and N_2 as a carrier gas. The used catalyst was washed with benzene and dried; then it was reused for the epoxidation for testing the catalyst reusability.

The conversion, product selectivity and product yield were calculated as follows: conversion (%) = [(moles of reactant converted) × 100]/[moles of reactant in feed], product selectivity (%) = [(moles of product formed) × 100]/[moles of reactant converted] and product yield (%) = (percentage of reactant converted to a particular product) or [conversion (%) × product selectivity (%)/100].

3. Results and discussion

3.1. Characterization of the catalysts

The supports have been characterized for their surface area and basicity and the supported gold catalysts for their gold loading, gold particle size and morphology, surface area and surface species. Results of the support and catalyst characterizations are presented in Figs. 1 and 2 and Tables 1 and 2. The values of the standard reduction potentials for the supports are also included in Table 1. High gold loading on the supports was achieved when the catalysts were prepared by the HDP method. The observed gold loading on Al_2O_3 and Tl_2O_3 was much lower, however, when the gold was deposited on these supports by the DP method. The fact that the gold loading achieved by the HDP method was higher than that achieved by the DP method is consistent with that observed earlier for Au/TiO_2 catalysts [16,19]. Both the gold

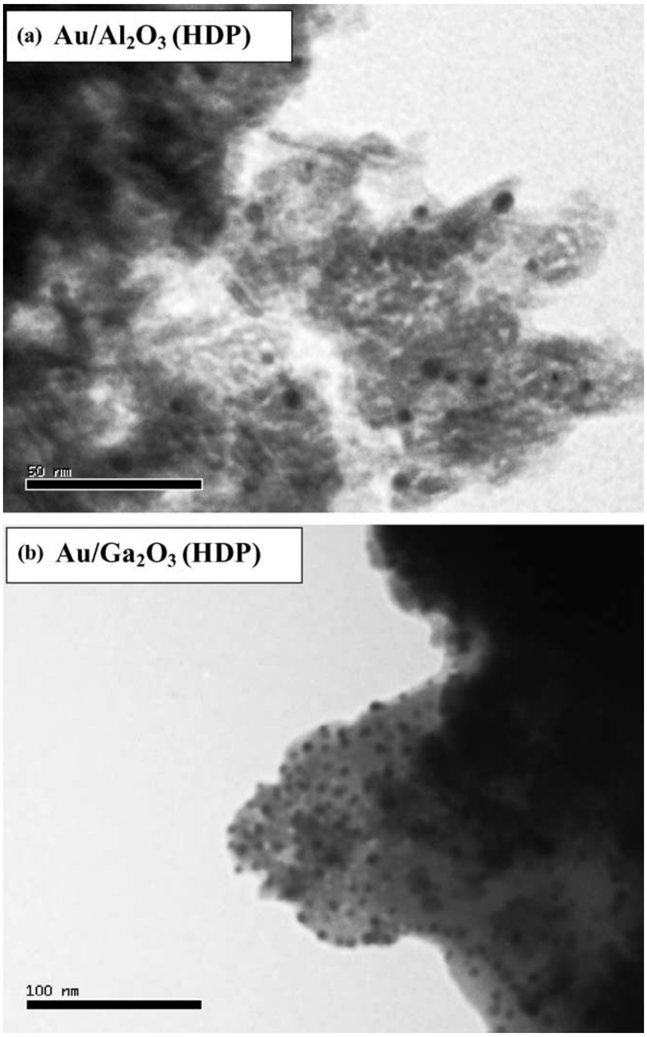

Fig. 1. HRTEM of (a) Au/Al$_2$O$_3$ (HDP) and (b) Au/Ga$_2$O$_3$ (HDP).

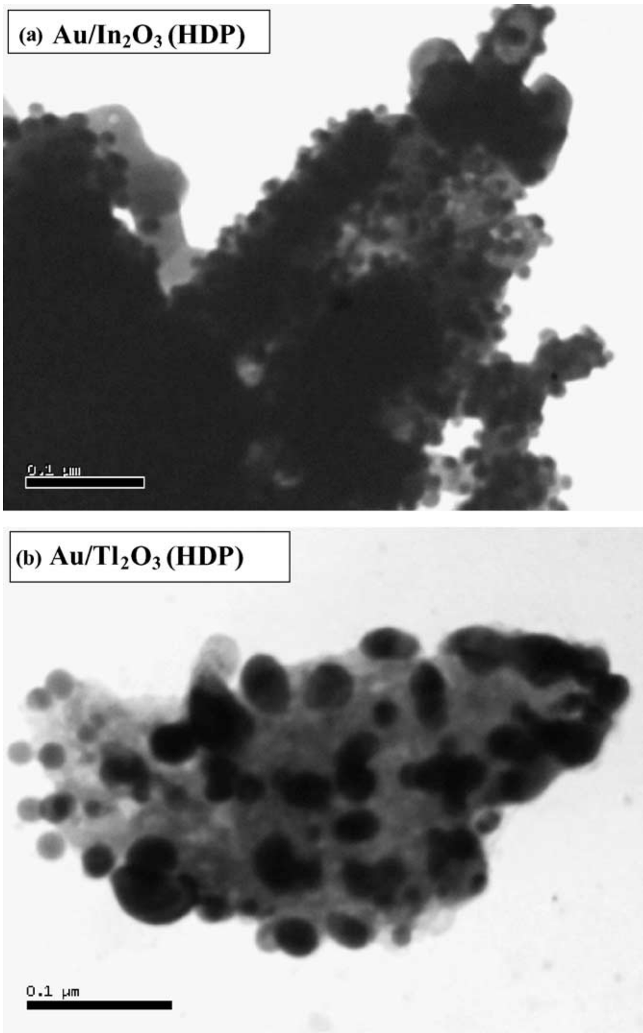

Fig. 2. HRTEM of (a) Au/In$_2$O$_3$ (HDP) and (b) Au/Tl$_2$O$_3$ (HDP).

loading and the particle size observed for the different supports are in the following order: $Al_2O_3 < Ga_2O_3 < In_2O_3 < Tl_2O_3$.

A comparison of the gold loading and Au particle size data with the support properties (Table 1) leads to the following important observations:

- Both the Au loading and Au particle size are increased with the decrease in the support surface area. The increase in the Au particle size is expected because of the increase in the Au loading for the support having smaller and smaller surface area for the Au dispersion. However, the increase in the Au loading is unusual; it may be attributed to other surface properties of the supports.
- Both the gold loading and Au particle size are increased with increasing the basicity of support (measured in terms of the pH of support–water slurry) and also with increasing the standard reduction potential. This reveals a close relationship between the gold loading and the basicity and/or standard reduction potential of the support. It is interesting to note that the gold loading in thallium oxide is the same as that (8.0 wt.%) expected when there is a complete deposition of gold from the solution.
- In the cases of the Al$_2$O$_3$ and Ga$_2$O$_3$ supports, the catalyst surface area is decreased after the gold deposition. However, for the In$_2$O$_3$ and Tl$_2$O$_3$ supports, the catalyst surface area is increased after the gold deposition. The changes in the surface area are expected because of the rehydroxylation of the supports during the gold deposition, followed by calcination of the hydroxylated gold containing supports.

The increase in the gold particle size with decreasing the support surface area and/or increasing the metal loading is consistent with the trends observed earlier [18]. With increasing the basicity of supports, the pH at the support solution interface is increased, resulting in more precipitation of hydroxylated gold species on the support surface because of the increased OH$^-$ ion concentration at the interface. Since the isoelectric point (or point of zero charge)

Table 1
Preparation and characterization of the Gr. IIIa metal oxide supports and supported gold catalysts

Support	pH of support–water slurry[a]	Method of Au deposition	Au loading (wt.%)	Surface area		Au particle size (nm)	Gold dispersion[b] (%)	Standard electrode potential (v)
				Support	Catalyst			
Al_2O_3	5.2	HDP	6.36	209	147.4	4.1 ± 2.3	2.8	$E(Al^{3+}/Al^0) = -1.66$
Ga_2O_3	7.2	HDP	6.43	21.8	17.4	6.6 ± 3.7	1.7	$E(Ga^{3+}/Ga^0) = -0.53$
In_2O_3	8.9	HDP	6.81	3.3	3.5	15.6 ± 6.3	0.7	$E(In^{3+}/In^0) = -0.34$, $E(In^{3+}/In^{1+}) = -0.44$
Tl_2O_3	12.6	HDP	8.00	< 0.5	1.7	24.4 ± 13.1	0.5	$E(Tl^{3+}/Tl^0) = +0.72$, $E(Tl^{3+}/Tl^{1+}) = +1.25$
Al_2O_3	5.2	DP	2.10	209	169.3	n.d.	–	–
Tl_2O_3	12.6	DP	5.42	< 0.5	2.4	n.d.	–	–

n.d. = not determined.

[a] 0.1 g support in 10 ml distilled water.

[b] Gold dispersion calculated using the equation $D = 6(v_{\mathrm{m}} + a_{\mathrm{m}})/d_{v\mathrm{A}}$, assuming spherical Au particles.

for the hydrated Gr. IIIa metal oxides is expected to increase as the atomic number of the Gr. IIIa metal increases [20], the amount of $AuCl_4^-$ anions adsorbed on the positively charged metal oxide surface during the gold deposition is also expected to follow the following order for the metal oxides: $Al_2O_3 < Ga_2O_3 < In_2O_3 < Tl_2O_3$.

The observed dependence on the standard reduction potential of the gold loading may be attributed to the oxidation–reduction reactions between the adsorbed Au(III) species and the metal oxides at the liquid–solid interface. This is consistent with the earlier observation that an adsorption of gold chloride on oxidizable mineral oxides leads to the reduction of Au(III) to metallic gold (Au^0), which is deposited on the metal oxide supports [16,21]. Indeed, in the thallium oxide-supported gold catalyst, the thallium oxide is found to exist mainly as Tl_2O_3, with traces of Tl_2O; the easily oxidizable Tl_2O might have been oxidised by Au(III) to Tl_2O_3, resulting in a larger Au deposition on the support.

The Au/Al_2O_3 and Al/In_2O_3 catalysts were also characterised for their surface species by XPS. The XPS data for the two catalysts are presented in Table 2. In the case of Au/Al_2O_3 catalyst, a single XPS peak corresponding to the binding energy of 335.0 eV was observed for $Au4d_5$ electron (in this case, because of the overlapping problems, the XPS for $Au4f_5$ or $Au4f_7$ could not be obtained). The single binding energy value indicates the presence of only metallic gold (Au^0) on the alumina surface. Also, only a single XPS peak (BE = 74.1 eV) for Al2p electron is observed, indicating the presence of aluminium only in one oxidation state (Al^{3+}) on the surface. However, in case of the Au/In_2O_3 catalyst, two XPS peaks corresponding to the binding energies of 86.5 and 88.3 eV (with 1.8 eV shift), were observed for $Au4f_5$ electron (two XPS peaks were also observed for the $Au4f_7$ electron). This clearly indicates the presence of both the metallic and ionic gold species (viz. Au^0 and Au^{3+}) on the In_2O_3 surface. Very recently, the presence of both metallic gold and ionic gold species in a Au/CeO_2 catalyst has also been observed [22]. It is interesting to note from the XPS data (Table 3) that there is a shift of 1.1 eV for the $In3d_3$ electron (which has two binding energies, 452.1 and 453.2 eV) for the Au/In_2O_3, but no shift for the Al2p electron (which has only one binding energy, 74.1 eV) for the Au/Al_2O_3. These observations reveal that, while the Al_2O_3 is not reduced because of its much lower standard reduction potential ($E(Al^{3+}/Al^0) = -1.66$ V), the In_2O_3 ($E(In^{3+}/In^0) = -0.34$ V) exists in both the fully oxidised (In^{3+}) and reduced forms (probably In^{1+} or In^{2+}) forms at the catalyst surface. In the case of the Au/In_2O_3 catalyst, the binding energy shift for O1s (1.4 eV) is also much larger than that for the Au/Al_2O_3 (0.6 eV), which also indicates the presence of two different indium oxide species on the Au/In_2O_3. The observed lower O1s binding energy for the Au/In_2O_3 catalyst also indicates that the catalyst is more basic in nature than the Au/Al_2O_3 catalyst.

Because of the high toxicity of thallium oxide, XPS data for the Au/Tl_2O_3 was not obtained. XRD analysis of the

Table 2
XPS data for the Au/Al_2O_3 and Au/In_2O_3 catalysts

Catalyst	Binding energy (eV)[a]				
	O1s	Al2p	$In3d_3$	$Au4d_5$	$Au4f_5$
Au/Al_2O_3	531.3				
	531.9	74.1	–	335.0	–
	(0.6 eV shift)				
Au/In_2O_3	531.5	–	452.1	–	86.5
	530.1		453.2		88.3
	(1.4 eV shift)		(1.1 Ev shift)		(1.8 eV shift)

[a] Binding energies are based on the assumption of C1s binding energy of 285 eV.

Table 3
Results of the epoxidation of styrene over the Au/Al_2O_3 and Au/Tl_2O_3 catalysts prepared by the DP method

	Au/Al_2O_3	Au/Tl_2O_3
Conversion of styrene (%)	7.3	60.5
Conversion of TBHP (%)	22.0	44.8
Product selectivity (%)		
Styrene oxide	<1	56.9
Benzaldehyde	3.7	7.6
Phenyl acetaldehyde	<1	22.3
Other products[a]	>94.0	13.2

[a] Benzoic acid and phenyl acetic acid.

Au/Tl_2O_3 showed the presence of Tl_2O_3 (major), metallic gold (Au^0) and Tl_2O_3 (trace) phases in the catalyst.

3.2. Epoxidation of styrene

Results showing the influence of Gr. IIIa metal oxide support on the conversion and product selectivity in the epoxidation of styrene by anhydrous TBHP over the supported gold catalysts prepared by the HDP method are presented in Fig. 3. The results over the Au/Al_2O_3 and Au/Tl_2O_3 catalysts prepared by the DP methods are given in Table 3. Also the epoxidation results over the metal oxide supports alone (i.e. without gold deposition) are presented in Fig. 4. A comparison of the epoxidation performance of the supported gold catalysts prepared by the two methods (Table 3 and Fig. 3) leads to the following important observations:

- Both the activity (styrene conversion) and the selectivity for styrene oxide and phenyl acetaldehyde of the catalysts are in the following order: $Au/Al_2O_3 < Au/Ga_2O_3 < Au/In_2O_3 < Au/Tl_2O_3$. The catalyst order for the selectivity of benzaldehyde and other products (benzoic acid and phenyl acetic acid) is the opposite one.
- The performance of the Au/Al_2O_3 (HDP) is superior to that of the Au/Al_2O_3 (DP); the latter showed not only very poor activity but also almost no selectivity for the epoxide. The Au/Tl_2O_3 (DP) showed values comparable to those of the Au/Tl_2O_3 (HDP), even though the Au loading in the former is lower (5.4 wt.%) (Table 1).
- The trends for the catalytic activity and the epoxide selectivity of the gold catalysts prepared by the two methods are quite similar to the trends for their basicity and standard reduction potential (Table 1), indicating some sort of correlation between the epoxidation performance (conversion and selectivity) and the properties (viz. basicity and/or redox properties) of the supported Au catalysts.
- The ratio of moles of TBHP consumed per mole of styrene converted is high (≥ 3.0) for the Au/Al_2O_3, Au/Ga_2O_3 and Au/In_2O_3 catalysts; it is nearly the stoichiometric one (1.08) for the Au/Tl_2O_3 catalyst (HDP or DP). The supported Au catalysts also show the same trend for their performance when the epoxidation was carried out for a shorter period (2 h); the styrene conversion and the epoxide selectivity for the Au/Al_2O_3, Au/Ga_2O_3, Au/In_2O_3 and Au/Tl_2O_3 catalysts prepared by the HDP method were 33.5 and 22.0, 35.0 and 24.1, 37.9 and 36.3 and 52.0 and 49.3%, respectively.

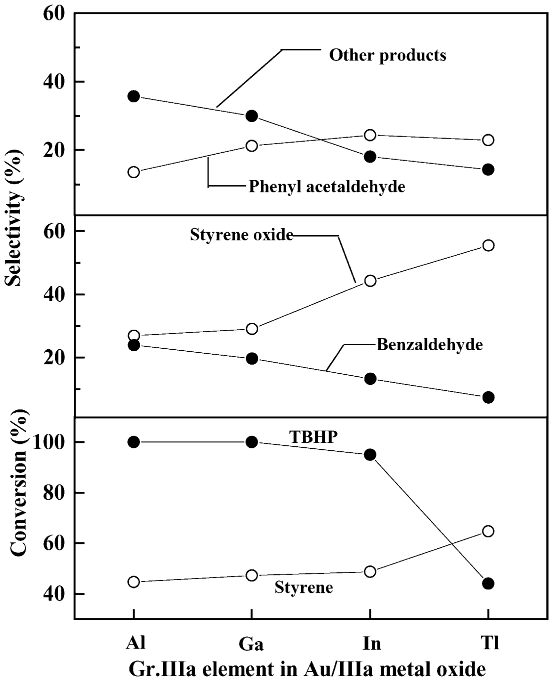

Fig. 3. Influence of Gr. IIIa elements present in the Gr. IIIa metal oxide-supported Au catalysts on their performance in the epoxidation of styrene.

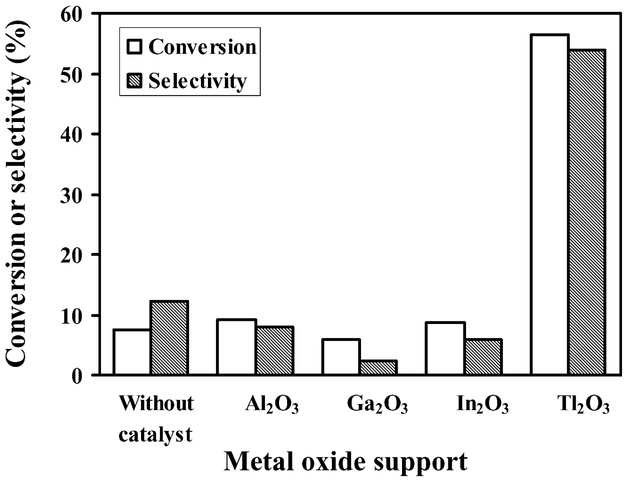

Fig. 4. Performance of Gr. IIIa metal oxide supports (without gold) in the epoxidation of styrene.

The observed high TBHP consumption for the Au/Al_2O_3, Au/Ga_2O_3 and Au/In_2O_3 catalysts (Fig. 3) is due to the formation of benzaldehyde and higher oxidation products (viz. benzoic acid and phenyl acetic acid) with higher selectivity and also due to the decomposition of TBHP $[(CH_3)_3COOH \rightarrow (CH_3)_3COH + 0.5O_2]$. When the supports alone (Al_2O_3, Ga_2O_3 and In_2O_3) were impregnated with 0.1 wt.% HCl and calcined at 400 °C, the chlorinated Al_2O_3, Ga_2O_3 and In_2O_3 supports showed 8.1, 6.2 and 8.9% styrene conversion, respectively, with almost no selectivity for styrene oxide; the only product formed was benzoic acid. This observation clearly indicates the positive role played by the gold deposited on these supports for the observed good styrene oxide selectivity, in spite of the presence of chloride anions (which are not removed during the washing of the catalyst after the gold deposition on the supports).

The observed very poor performance of the Au/Al_2O_3 (DP) catalyst (Table 3) is mostly attributed to a much lower gold loading on the alumina support (Table 1). It may also be due to the presence of traces of Na^+ cations on the catalyst surface, even after careful and thorough washing of the catalyst by deionized water, after the gold deposition by the DP method [23]. However, even though the Au loading for the Au/Tl_2O_3 (DP) is lower than that for the Au/Tl_2O_3 (HDP), the performances of both the catalysts are comparable. This observation and the earlier observed good activity of alumina in the epoxidation of styrene by anhydrous H_2O_2 [9], prompted us to study the activity of supports alone in the epoxidation of styrene by anhydrous TBHP (Fig. 4).

The results in Fig. 4 clearly reveal that the Al_2O_3, Ga_2O_3 and In_2O_3 supports show almost no activity in the epoxidation. They show even less epoxide selectivity than that obtained in the absence of any catalyst (the reaction products formed over these supports are mainly the secondary oxidation products—benzoic acid and phenyl acetic acid). On the contrary, the Tl_2O_3 support itself shows both high activity and selectivity in the epoxidation. This is the reason why the Au/Tl_2O_3 catalysts prepared by both the DP and HDP methods showed a comparable performance in the epoxidation even though the Au loading in the catalyst was different. The TBHP conversion over the Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3 supports in the epoxidation was 10.0, 30.4, 41.8 and 44.7, respectively. In the case of Tl_2O_3 support as the catalyst also, the TBHP consumed per mole of styrene converted is much smaller than that observed for the other supports. The high epoxidation activity of the Tl_2O_3 and Au/Tl_2O_3 catalysts seems to be attributed to both its very high basicity and reducibility (i.e. high value of standard reduction potential, $E(Tl^{3+}/Tl^{+1}) = +1.25$ V and $E(Tl^{3+}/Tl^0) = +0.72$ V); in the Au/Tl_2O_3 catalyst, the Au has only a little role to play. The epoxidation over Tl_2O_3 may involve a redox mechanism. However, further detailed work is necessary to understand the reaction mechanism. Nevertheless, thallium oxide is highly toxic and hence its use as a catalyst or in the catalyst for the epoxidation is very much limited because of its high toxicity.

Among the Au/Al_2O_3, Au/Ga_2O_3 and Au/In_2O_3 catalysts (prepared by HDP method), the Au/In_2O_3 catalyst showed the best performance and also excellent reusability in the epoxidation (in the third reuse of the catalyst, the conversion and styrene oxide selectivity were found to be 51 and 48%, respectively). The epoxidation activity of the supported gold catalysts is attributed to the gold species, particularly the low coordinated Au atoms at the corners and edges of nano-size gold particles [24–26] and cationic gold species (Au^{3+}) and also to the basicity and/or redox properties of the support used in the catalysts. Earlier studies also showed a marked increase in the epoxide selectivity because of the presence of a base in the epoxidation of styrene by H_2O_2 over TS-1 and Al_2O_3 [9,27].

The styrene oxide selectivity in the epoxidation of styrene by H_2O_2 over TS-1 and Ti/SiO$_2$ was found to be 2–6% [4,27] and 14–19% [3], respectively. The epoxidation selectivity of the supported gold catalysts (22–56%) is relatively very good.

4. Conclusions

From the present studies on the epoxidation of styrene by anhydrous TBHP over Au/Al_2O_3, Au/Ga_2O_3, Au/In_2O_3 and Au/Tl_2O_3, prepared by the HDP and DP methods, the following important conclusions have been drawn:

1. The HDP method provides the supported gold catalysts with much higher gold loading and also the catalysts prepared by this method show better performance in the epoxidation.
2. The gold loading, gold particle size and epoxidation performance of the supported gold catalysts are strongly influenced by the basicity and/or reduction properties of the support used in the catalyst. The order of catalysts for their gold loading, for Au particle size and for catalytic activity and/or epoxide selectivity in the epoxidation is as follows: $Au/Al_2O_3 < Au/Ga_2O_3 < Au/In_2O_3 < Au/Tl_2O_3$; the higher is the basicity and/or reduction potential, the higher are the Au loading, the particle size, and the epoxidation activity/selectivity of the catalyst. The Au/Tl_2O_3 catalyst is also a best choice for the epoxidation even from the point of view of the TBHP consumption.
3. The Al_2O_3, Ga_2O_3 and In_2O_3 supports alone show almost no activity in the epoxidation. However, the Tl_2O_3 support shows the epoxidation activity and selectivity comparable to that of the Au/Tl_2O_3 catalyst.
4. In case of the Au/Tl_2O_3 catalyst, its epoxidation activity/selectivity is attributed mostly to the high basic nature and/or redox properties of the Tl_2O_3 support. However, for the Au/A_2O_3, Au/Ga_2O_3 and Au/In_2O_3 catalysts, their epoxidation activity/selectivity is attributed to the gold species (neutral and/or ionic Au species) on the support and also to the acid–base properties of the support. Generally, the catalyst containing more basic support shows better performance in the epoxidation.
5. Both the neutral and ionic Au species (Au^0 and Au^{3+}) and also the indium in two different oxidation states are found to be present on the surface of Au/In_2O_3 catalyst. However, only the neutral Au species (Au^0) and aluminium in only a single oxidation state (Al^{3+}) are observed on the surface of Au/Al_2O_3.

Acknowledgments

Dr. B.S. Uphade and R. Jha are grateful to CSIR, New Delhi (India) for the award of Senior Research Associateship (SRA) and Senior Research Fellowship (SRF), respectively, and Mr. N.S. Patil is grateful to Royal Melbourne Institute of

Technology for a research fellowship. The authors are grateful to Prof. D.G. McCulloh and Aaron Torpy of the Department of Physics, RMIT, Melbourne, Australia, for their help in the HRTEM and XPS analyses.

References

[1] D. Swern (Ed.), Organic Peroxide, vol. 2, Wiley-Interscience, New York, 1971.

[2] V.R. Grieken, J.L. Sotelo, C. Martos, J.L.G. Fierro, M. Lopez-Granados, R. Mariscal, Catal. Today 61 (2000) 49.

[3] Q. Yang, S. Wang, J. Lu, G. Xiong, Z. Feng, X. Xin, C. Li, Appl. Catal. A Gen. 194–195 (2000) 507.

[4] Q. Yang, C. Li, J.L. Wang, P. Ying, X. Xin, W. Shi, Stud. Surf. Sci. Catal. 130 (2000) 221.

[5] S.B. Kumar, S.P. Mirajkar, G.C.G. Pais, P. Kumar, R. Kumar, J. Catal. 156 (1995) 163.

[6] S.C. Laha, R. Kumar, J. Catal. 204 (2001) 64.

[7] W. Zhang, M. Froba, J. Wang, P. Tanev, J. Wong, T.J. Pinnavaia, J. Am. Chem. Soc. 118 (1996) 9164.

[8] J. Fu, D. Yin, Q. Li, L. Zhang, Y. Zhang, Micropor. Mesopor. Mater. 29 (1999) 351.

[9] V.R. Choudhary, N.S. Patil, S.K. Bhargava, Catal. Lett. 89 (2003) 55.

[10] C. Coperet, H. Adolfson, K.B. Sharpless, Chem. Commun. (1997) 1565.

[11] E.E. Strangland, K.B. Stavens, R.P. Andres, W.N. Delgass, J. Catal. 199 (2000) 332.

[12] A. Zwijnenburg, M. Saleh, M. Makkee, J.A. Moulijn, Catal. Today 72 (2002) 59.

[13] B.S. Uphade, T. Akita, T. Nakamura, M. Haruta, J. Catal. 209 (2002) 331.

[14] H.H. Willard, N.K. Tang, Ind. Eng. Chem. Anal. Ed. 9 (1937) 357.

[15] K. Tanabe, M. Itoh, K. Morishige, H. Hattori, in: B. Delmon, P.A. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts I, Elsevier, Amsterdam, 1969, p. 65.

[16] R. Zanella, S. Giorgio, C.R. Henry, C. Louis, J. Phys. Chem. B 106 (2002) 7634.

[17] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda, Y. Nakahara, Stud. Surf. Sci. Catal. 72 (1991) 695.

[18] N.S. Patil, B.S. Uphade, P. Jana, R.S. Sonawane, S.K. Bhargawa, V.R. Choudhary, Catal. Lett. 94 (2004) 89.

[19] H. Sakurai, M. Haruta, Catal. Today 29 (1998) 361.

[20] G.A. Parks, Chem. Rev. 65 (1965) 177.

[21] C. Greffie, M.F. Benedetti, C. Parron, M. Amouric, Geochim. Cosmochim. Acta 60 (1996) 1531.

[22] Q. Fu, H. Saltburg, M. Flytzani-Stephanopoulos, Science 301 (2003) 935.

[23] B.S. Uphade, S. Tsubota, T. Hayashi, M. Haruta, Chem. Lett. (1998) 1277.

[24] N. Lopez, J.K. Norskov, J. Am. Chem. Soc. 124 (2002) 11262.

[25] L.M. Molina, B. Hammer, Phys. Rev. Lett. 90 (2003) 206102–206111.

[26] J.A. Rodriquez, M. Perez, T. Jirsak, J. Evans, J. Hrbek, L. Gonzalez, Chem. Phys. Lett. 378 (2003) 526.

[27] S.C. Laha, R. Kumar, J. Catal. 204 (2001) 64.